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<b>(54) Title:</b> EMULSIFICATION SYSTEM FOR LIGHT FUEL OIL EMULSIONS  <b>(57) Abstract</b>  The present invention relates to a fuel oil composition useful for controlling the emission of nitrogen oxides from turbines. The composition comprises an emulsion formed from water and a light fuel oil, the emulsion further comprising an emulsification system which comprises an alkanolamide; a phenolic surfactant; and, optionally, a difunctional block polymer terminating in a primary hydroxyl group.		

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## DESCRIPTION

## EMULSIFICATION SYSTEM FOR LIGHT FUEL OIL EMULSIONS

Technical Field

5 The present invention relates to a fuel oil composition which comprises an emulsion of water and a light fuel oil with an emulsification system comprising an alkanolamide, a phenolic surfactant, and, optionally, a difunctional block polymer. By forming the described emulsion, improvements are obtained in the combustion efficiency of the fuel oil in order to reduce the emissions of nitrogen oxides ( $\text{NO}_x$ , where x is an integer, generally 1 or 2), and visible emissions (particulates, which lead to plume opacity) to the atmosphere.

15 Stationary and mobile combustion units have been identified as sources of nitrogen oxides emissions to the atmosphere. Electric power generating utilities, in fact, have been identified as a prime contributor of  $\text{NO}_x$  emissions. Nitrogen oxides can form from the combustion of organic and inorganic nitrogen compounds in fuel and, at higher temperatures, from thermal oxidation of nitrogen in combustion air. Combustion or gas turbines are considered to be even more prone to generate  $\text{NO}_x$  because of the "favorable" high temperature and

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pressure conditions existing therein, as well as their more oxidative operating conditions.

Nitrogen oxides are troublesome pollutants and comprise a major irritant in smog. It is further  
5 believed that nitrogen oxides can cause or enhance the process known as photochemical smog formation through a series of reactions in the presence of sunlight and hydrocarbons. Moreover, nitrogen oxides are a  
10 significant contributor to acid rain and have been implicated in the undesirable warming of the atmosphere through what is known as the "greenhouse effect" and in the depletion of the ozone layer. In addition, gas turbines often emit a visible plume which is highly undesirable since it causes concern among the general  
15 population in areas surrounding the facility.

In the past, direct water injection into the combustion chamber of a stationary electric power generating source has been utilized to reduce  $\text{NO}_x$  by lowering the peak flame temperatures. This can be  
20 effective at achieving substantial  $\text{NO}_x$  reductions. The use of direct water injection, though, has several disadvantages, including water feed rates which can reach 1.5 x fuel rates or higher, high installation costs, and high energy loss due to cooling. Furthermore, the direct  
25 addition of water may involve thermal shock which can cause thermal contraction and cracking of the liners in the combustion box.

The emulsification of heavy (i.e., residual or #6) fuel oils with water prior to combustion has been  
30 suggested to induce a "micro explosion" to improve

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combustion efficiency. Emulsification systems for heavy fuel oils, though, have been found to be unsuccessful at emulsifying lighter grades of fuel oil. It is believed this is because the heavy fuel oils comprise a high  
5 viscosity grade of oil rich in polynuclear aromatic and long chain polymeric hydrocarbons. The high aromatic content and, therefore, polar nature of the heavy fuel oils make them amenable to emulsification by a large variety of conventional polar surfactants.

10 Contrariwise, lighter fuel oils such as #1 oil, #2 oil, or #4 oil comprise much lower boiling fractions than the heavy fuel oils. Light fuel oils contain very little to almost no aromatic compounds and consist of relatively low molecular weight aliphatic and naphthenic  
15 hydrocarbons. It is well documented that many surfactants are not readily soluble in naphthenic/aliphatic hydrocarbons such as kerosene. Because of this, such hydrocarbons are not readily emulsified by many classes of surfactants, such as nonylphenol  
20 ethoxylates or ethoxylated sugars, which have been found to be of limited effectiveness when used alone and which have little or no solubility in aliphatic hydrocarbons such as kerosene (#1 fuel oil). Because of this dichotomy in chemical properties, different emulsifier  
25 chemistries are needed when emulsions are formed using lighter fuel oils.

Although emulsifiers for water and fuel oil emulsions have, in the past, been described, such as ethoxylated nonylphenols and the like, disclosed by Puttock and  
30 Somerville in U.S. Patent 5,000,757, suitable systems for maintaining a superior water and light fuel oil emulsion have not been adequately disclosed.

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What is desired, therefore, is an emulsification system for water and light fuel oil emulsions which, when combusted, may absorb heat required to rapidly flash the water to steam which to reduce peak flame temperature and thus control thermal  $\text{NO}_x$  formation; and also lead to improved atomization and thereby improve fuel combustion.

#### Disclosure of Invention

The present invention relates to a water and fuel oil emulsion for reducing nitrogen oxides emissions and improving combustion efficiency in a stationary, electric powered generating source, especially a gas turbine (the term "gas turbine" will be considered to be interchangeable with the term "combustion turbine" for the purposes of this disclosure). In particular, this invention relates to a stable water and light fuel oil emulsion. The subject emulsion can be either a water-in-fuel oil or a fuel oil-in-water emulsion, although water-in-fuel oil emulsions are generally preferred for most applications and can be used as the fuel for a gas turbine.

The oil phase in the inventive emulsions comprises a light crude naphtha fuel oil by which is meant a fuel oil having little or no aromatic compounds and consisting essentially of relatively low molecular weight aliphatic and naphthenic hydrocarbons. In the refining arts, light crude naphtha refers specifically to the first liquid distillation fraction, which has a boiling range of about 90°F to about 175°F. This is distinguished from heavy crude naphtha, which is the second distillation fraction, with a boiling range of about 325°F to about 425°F. "Naphthenic" is an industrial term which refers to fully saturated cyclic hydrocarbons having the general formula  $\text{C}_n\text{H}_{2n}$ . "Aliphatic" is an industrial term which

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refers to fully saturated linear hydrocarbons having the general formula  $C_nH_{2n+2}$ .

Suitable fuels are those having a viscosity of about 5 SSF to about 125 SSF, preferably about 38 SSF to about 100 SSF, at 100°F and a specific gravity of about 0.80 to about 0.95 at 77°F. Such fuels include fuels conventionally known as diesel fuel, distillate fuel, #2 oil, or #4 oil, as defined by the American Society of Testing and Measurement (ASTM) standard specification for fuel oils (designation D 396-86). Especially preferred are distillate fuels. Included among these are kerosene (or ASTM grade no. 1 fuel oil) and jet fuels, both commercial and military, commonly referred to as Jet-A, JP-4 and JP-5.

The subject emulsions advantageously comprise water-in-fuel oil emulsions having up to about 95% water by weight. The emulsions which have the most practical significance in combustion applications are those having about 5% to about 50% water and are preferably about 10% to about 35% water-in-fuel oil by weight. In addition, it is recognized that as the amount of the discontinuous phase (i.e., the water in a water-in-fuel oil emulsion) increases, the possibility of inversion arises. For instance, in an emulsion containing up to about 65% water-in-fuel oil, inversion will cause the emulsion to become a fuel oil-in-water emulsion comprising about 35% of the oil phase.

Although demineralized water is not required for successful control of nitrogen oxides and opacity, the use of demineralized water in the emulsion formed according to the process of this invention is preferred in order to avoid the deposit of minerals from the water

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on the blades and other internal surfaces of the gas turbine. In this way, turbine life is extended and maintenance and outage time significantly reduced.

The inventive emulsions are prepared such that the  
5 discontinuous phase preferably has a particle size wherein at least about 70% of the droplets are below about 5 microns Sauter mean diameter. More preferably, at least about 85%, and most preferably at least about 90%, of the droplets are below about 5 microns Sauter  
10 mean diameter for emulsion stability.

Emulsion stability is largely related to droplet size. The primary driving force for emulsion separation is the large energy associated with placing oil molecules in close proximity to water molecules in the form of  
15 small droplets. Emulsion breakdown is controlled by how quickly droplets coalesce. Emulsion stability can be enhanced by the use of surfactants and the like, which act as emulsifiers or emulsion stabilizers. These generally work by forming repulsive layers between  
20 droplets prohibiting coalescence.

The gravitational driving force for phase separation is much more prominent for large droplets, so emulsions containing large droplets separate most rapidly. Smaller droplets also settle, but can be less prone to  
25 coalescence, which is the cause of creaming. If droplets are sufficiently small, the force of gravity acting on the droplet is small compared to thermal fluctuations or subtle mechanical agitation forces. In this case the emulsion can become stable almost indefinitely, although  
30 given a long enough period of time or a combination of thermal fluctuations these emulsions will eventually separate.



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Although it is possible to emulsify the water and light fuel oil and inject directly into the combustion can or other combustion zone, generally it is required that water and light fuel oil emulsions exhibit a high degree of stability. For instance, since gas turbines are often operated as "peaking" units which do not operate regularly, an emulsified fuel may sit stagnant for extended periods or with only mild recirculation in the fuel line. To avoid separation of the emulsion, which can cause slugs of water to be injected through the burner nozzle leading to combustion problems and possible engine damage, an emulsification system must be employed to maintain the emulsion.

Advantageously, the emulsification system utilized comprises about 25% to about 85% by weight of an amide, especially an alkanolamide or n-substituted alkyl amine; about 5% to about 25% by weight of a phenolic surfactant; and about 0% to about 40% by weight of a difunctional block polymer terminating in a primary hydroxyl group. More preferably, the amide comprises about 45% to about 65% of the emulsification system; the phenolic surfactant about 5% to about 15%; and the difunctional block polymer about 30% to about 40% of the emulsification system.

Suitable n-substituted alkyl amines and alkanolamides which can function to stabilize the emulsion of the present invention are those formed by the condensation of, respectively, an alkyl amine and an organic acid or a hydroxyalkyl amine and an organic acid, which is preferably of a length normally associated with fatty acids. They can be mono-, di-, or triethanolamines and include any one or more of the following: oleic diethanolamide, cocamide diethanolamine (DEA), lauramide DEA, polyoxyethylene (POE) cocamide, cocamide monoethanolamine (MEA), POE lauramide DEA, oleamide DEA,

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linoleamide DEA, stearamide MEA, and oleic triethanolamine, as well as mixtures thereof. Such alkanolamides are commercially available, including those under trade names such as Clindrol 100-0, from Clintwood Chemical Company of Chicago, Illinois; Schercomid ODA, 5 from Scher Chemicals, Inc. of Clifton, New Jersey; Schercomid SO-A, also from Scher Chemicals, Inc.; and Mazamide®, and the Mazamide series from PPG-Mazer Products Corp. of Gurnee, Illinois.

10 The phenolic surfactant is preferably an ethoxylated alkyl phenol such as an ethoxylated nonylphenol or octylphenol, especially ethylene oxide nonylphenol which is available commercially under the tradename Triton N from Union Carbide Corporation of Danbury, Connecticut 15 and Igepal CO from Rhone-Poulenc Company of Wilmington, Delaware.

The block polymer which is an optional element of the emulsification system of the present invention advantageously comprises a nonionic, difunctional block 20 polymer which terminates in a primary hydroxyl group and has a molecular weight ranging from about 1,000 to above about 15,000. Such polymers are generally considered to be polyoxyalkylene derivatives of propylene glycol and are commercially available under the tradename Pluronic 25 from BASF-Wyandotte Company of Wyandotte, New Jersey. Preferred among these polymers are propylene oxide/ethylene oxide block polymers commercially available as Pluronic 17R1.

30 In addition to the noted components, the emulsification system of the present invention may further comprise up to about 30% and preferably about 10 to about 25% of a light crude naphtha fuel oil, most

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preferably the light crude naphtha fuel oil which comprises the continuous phase of the inventive emulsion. It has been found that inclusion of the fuel oil in the emulsification system can in some cases increase emulsion stability of the emulsion itself. In addition, other components such as salts of alkylated sulfates or sulfonates such as sodium lauryl sulfate and alkanolamine sulfonates may also be included in the inventive emulsification system.

The use of the noted emulsification system provides chemical emulsification, which is dependent on hydrophylic-lipophylic balance (HLB), as well as on the chemical nature of the emulsifier. The HLB of an emulsifier is an expression of the balance of the size and strength of the hydrophylic and the lipophylic groups of the composition. The HLB system, which was developed as a guide to emulsifiers by ICI Americas, Inc. of Wilmington, Delaware can be determined in a number of ways, most conveniently for the purposes of this invention by the solubility or dispersability characteristics of the emulsifier in water, from no dispersability (HLB range of 1-4) to clear solution (HLB range of 13 or greater).

The emulsifiers useful in the present invention should most preferably have an HLB of 8 or less, meaning that after vigorous agitation they form a milky dispersion in water (HLB range of 6-8), poor dispersion in water (HLB range of 4-6), or show no dispersability in water (HLB range of less than 4). Although the precise explanation is unknown, it is believed that the inventive emulsification system provides superior emulsification because it comprises a plurality of components of different HLB values. Desirably, the emulsification

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system has a combined HLB of at least about 4.0, more preferably about 5.1 to about 7.0 to achieve this superior emulsification.

For instance, an emulsification system which  
5 comprises 70% oleic diethanolamide (average HLB 6), 10% ethylene oxide nonylphenol (average HLB 13), and 20% #2 fuel oil has a combined HLB of about 5.5 ( $70\% \times 6$  plus  $10\% \times 13$ ). An emulsification system which comprises 50% oleic diethanolamide, 15% ethylene oxide nonylphenol and  
10 35% of a propylene oxide/ethylene oxide block polymer (average HLB 2.5) has a combined HLB of about 5.8 ( $50\% \times 6$  plus  $15\% \times 13$  plus  $35\% \times 2.5$ ). Such emulsification systems would provide superior emulsification as compared with an emulsifier comprising 80% oleic diethanolamine  
15 and 20% #2 fuel oil, which has an HLB of about 4.8 ( $80\% \times 6$ ).

Desirably, the emulsification system of the present invention should be present at a level which will ensure effective emulsification. Preferably, the emulsification  
20 system is present at a level of at least about 0.05% by weight of the emulsion to do so. Although there is no true upper limit to the amount of the emulsification system which is present, with higher levels leading to greater emulsification and for longer periods, there is  
25 generally no need for more than about 5.0% by weight, nor, in fact, more than about 3.0% by weight.

It is also possible to utilize a physical emulsion stabilizer in combination with the emulsification system noted above to maximize the stability of the emulsion  
30 achieved in the process of the present invention. Use of physical stabilizers also provides economic benefits due to their relatively low cost. Although not wishing to be

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bound by any theory, it is believed that physical stabilizers increase emulsion stability by increasing the viscosity of immiscible phases such that separation of the oil/water interface is retarded. Exemplary of  
5 suitable physical stabilizers are waxes, cellulose products, and gums such as whalen gum and xanthan gum.

When utilizing both the emulsification system and physical emulsion stabilizers, the physical stabilizer is present in an amount of about 0.05% to about 5% by weight  
10 of the combination of chemical emulsifier and the physical stabilizer. The resulting combination emulsifier/stabilizer can then be used at the same levels noted above for the use of the emulsification system.

The emulsification provided must be sufficient to  
15 maintain the emulsion to a greater extent than if the emulsification system was not present and to as great an extent as possible. The actual level of emulsification will vary depending upon the percentage of oil and water in the emulsion and the particular fuel oil utilized.  
20 For example, when the continuous phase is #2 oil, it is highly desired that no more than about 0.1% water separation be present in the emulsion, and that the emulsion is maintained that way at ambient conditions for at least about two hours. Ambient conditions, that is,  
25 the conditions to which the emulsion is expected to be exposed, include the temperature in the gas turbine fuel feed lines. Such temperatures can be up to about 65°C, sometimes up to about 90°C and even as high as about 100°C for short periods of time.

30 The emulsion used in the process of the present invention can be formed using a suitable mechanical emulsifying apparatus which would be familiar to the

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skilled artisan. Advantageously, the apparatus is an in-line emulsifying device for most efficiency. The emulsion is formed by feeding both the water and the fuel oil in the desired proportions to the emulsifying apparatus, and emulsification system can either be admixed or dispersed into one or both of the components before emulsification or can be added to the emulsion after it is formed.

Preferably, the emulsification system is present at the time of emulsifying the water and fuel oil. Most advantageously, the emulsification system is provided in the water phase, depending on its HLB. It has been found that the emulsions noted above with the chemical emulsifiers can be stabilized at up to about 95% water-in-fuel oil or up to about 35% fuel oil-in-water. In fact, with mild agitation, such as recirculation, it is believed that the emulsions can stay in suspension indefinitely.

Surprisingly, the emulsion can then be introduced into the combustion can of the gas turbine through the fuel feed lines and burner nozzles conventionally used with such combustion apparatus. There is no need for modification of the gas turbine fuel feed lines or combustion can to accommodate the emulsion used in the process of this invention.

Although not wishing to be bound by any theory, it is believed that the use of an emulsion provides striking advantages over separate water injection systems because the water is being provided internal to the flame. By doing so, less water is required to achieve superior results, which reduces the deleterious effects of

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directly introducing large amounts of water to the combustion zone of the gas turbine.

Because of the advantages of introducing water internal to the flame, utilization of the inventive process results in a reduced use of demineralized water (since the emulsion contains less than the at least 1:1 ratio of water to fuel oil used when water is injected directly into the combustion can), and leads to less thermal stress which reduces maintenance cost and outage time.

When the emulsified fuel is introduced into the combustion zone, the heat of vaporization from the burning fuel causes the emulsified water droplets to become steam, which creates a secondary atomization. This secondary atomization improves combustion and increases the gas volume. In addition, the heat required to change the water to steam is believed to reduce the flame temperature of the combustion which helps to reduce formation of nitrogen oxides.

Additionally, use of the water/fuel oil emulsion can result in substantial elimination of the need for an expensive, independent smoke suppressant additive. Typically, such additives are heavy metal based products which can form deposits on the turbine blades, reducing efficiency and increasing maintenance costs. By the use of emulsions in the process of this invention, a 90% or greater reduction in smoke suppressant additive use has been achieved, which increases the blade life due to reduced deposits, and creates less wear on the turbine blade coatings. These advantages all lead to significant savings in operating and maintenance costs.

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Furthermore, when compared to a separate water injection system, the use of the process of this invention leads to improved engine fuel system integrity; the engine burns cooler, which, as noted, leads to less thermal stress; it is believed that the gas turbine can assume a higher load capacity; and compliance with environmental regulations is more easily obtainable.

In addition to its use as the sole fuel for a gas turbine, the emulsion of the present invention can also be used in a gas turbine which primarily fires natural gas, such as is taught by Brown and Sprague in U.S. Patent Application having Serial No. 07/751,170, entitled "Reducing Nitrogen Oxides Emissions by Dual Fuel Firing of a Turbine", filed August 28, 1991, the disclosure of which is incorporated herein by reference. By the use of a manifold which permits the dual injection of both natural gas and the inventive emulsion, it has been found that the nitrogen oxides content of the effluent can be substantially reduced when compared with the effluent when natural gas is fired alone. Although not fully understood, it is believed that the addition of the emulsion permits firing at a lower flame temperature due to the water introduction without the disadvantages of direct water injection into the combustion can.

The following examples further illustrate and explain the invention but are not considered limiting.

#### Example I

Emulsions of water in #2 fuel oil at water contents of 16.7%, 28.6%, 33.3%, and 41.2% by weight, respectively, are prepared by mixing the fuel oil and water for five minutes. When an emulsifier is present as noted below, it is used at a level of 0.1% for the 16.7%



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emulsion (Emulsion #1) and 0.2% for the remaining emulsions (Emulsions #2, #3, and #4, respectively). The mixture is then put in a manual Chase-Logeman brand hand homogenizer. The homogenizer is set at 1 1/2 turns open  
5 and homogenization conducted for sufficient time to pump 100 milliliters (ml) of liquid into a receiving flask.

Four samples of the emulsions are prepared; a first with no emulsifier to be used as a blank; a second with an emulsifier comprising 80% oleic diethanolamine and 20%  
10 #2 fuel oil (emulsifier 1) to be used as a control; a third with an emulsifier comprising 70% oleic diethanolamine, 10% ethylene oxide nonylphenol, and 20% #2 fuel oil (emulsifier 2); and a fourth with an emulsifier comprising 50% oleic diethanolamine, 15%  
15 ethylene oxide nonylphenol, and 35% of a propylene oxide/ethylene oxide block polymer commercially available as PLURONIC 17R1 (emulsifier 3).

After homogenization, 60 milliliters (mls) of each sample is placed into a beaker, to which is added 60 mls  
20 of #2 fuel oil. The resulting mixture is then mixed for ten minutes. A sample of each mixture is then placed in a 100 ml centrifuge tube and subjected to centrifugation for 15 minutes at 2500 revolutions per minute (rpm). Stability is determined by the amount of free water on  
25 the bottom of the centrifuge tube after centrifugation, and the amount of emulsification in the top fuel oil layer (distinguished by a darker and creamy appearance) or the amount of emulsified water layer (distinguished as a thick, white intermediate layer).

30 It is found that emulsifier 1 leads to an oil phase similar to the blank and a water phase comprising a large, white, creamy layer, whereas emulsifiers 2 and 3

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result in a large, cloudy layer in the oil phase and a water phase having a volume smaller to or similar to that of emulsifier 1. It is believed the cloudy oil layer of emulsifiers 2 and 3 indicates that water remains  
 5 stabilized within the oil after centrifugation in the form of a water-in-oil emulsion. In addition, emulsifiers 2 and 3 give better oil phase stability compared to the blank, whereas emulsifier 1 gives an oil phase stability similar to the blank.

10

Example II

An emulsion comprising 33% water in #4 fuel oil having a specific gravity of 0.885 at 77°F and a viscosity of 6 SSF at 122°F was formed according to the procedure detailed in Example 1 and divided into a blank  
 15 and three samples using 0.2% of emulsifiers 1, 2, and 3, respectively. The stability of the emulsions is tested by the centrifugation method described above and the results set out in Table 1.

TABLE 1

20		<u>% Free Water</u>	<u>% White* Emulsion</u>	<u>Other Observations</u>	<u>Total Emulsion</u>
	Blank	0.15	27	separation apparent	27%
25	Emulsifier 1	0.50	75 white	clear oil phase	75%
	Emulsifier 2	0.15	31 white	69% cloudy oil phase**	100%
	Emulsifier 3	0.15	35 white	65% cloudy oil phase	100%

30 \* oil in water emulsion

\*\* water in oil emulsion, generally considered more  
 desirable for inventive application

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Emulsifier 1 gave the largest volume (75%) of an emulsified water layer and higher, undesirable free water. The cloudiness in the oil phase observed with emulsifiers 2 and 3 is believed to be highly stable microemulsion droplets.

#### Example III

An emulsion comprising 43.2% water in #2 fuel oil is formed and divided into two samples, one comprising 0.2% of emulsifier 1 and the second comprising 0.2% of emulsifier 3. The emulsion is formed using an Emulsa brand in-line emulsifier available from Todd Combustion, Inc., of Stamford, Connecticut, with emulsion stability measured by centrifugation as described above. The results are set out in Table II, which illustrates the increased emulsification provided by emulsifier 3 over emulsifier 1 due to the presence of a mixed surfactant emulsification system.

#### TABLE II

20		<u>Appearance</u>		
		<u>% Oil</u>	<u>% Emulsion</u>	<u>% Water</u>
	Emulsifier 1	47	22	31
	Emulsifier 3	19	71	10

#### Example IV

The effect of varying levels of emulsifiers on diesel fuel, kerosene and #2 fuel oil emulsions is illustrated by forming emulsions according to the procedure detailed in Example I using emulsifier 2 at levels of 0.1%, 0.2%, and 0.4%. The results are set out in Table III (for diesel fuel), Table IV (for kerosene), and Table V (for

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#2 fuel oil).

Table IIIDiesel Fuel

	<u>% Water in Emulsion</u>	<u>% Emulsifier</u>	<u>% Emulsion</u>	<u>% Free Water</u>
5	5	0.1	99.75	0.25
	15	0.1	96.5	3.5
	45	0.1	77.0	23.0
	5	0.2	100.0	0
10	10	0.2	100.0	0
	15	0.2	97.7	2.3
	30	0.2	95.2	4.8
	5	0.4	100	0
15	10	0.4	99.95	0.05
	15	0.4	99.95	0.05
	30	0.4	100.0	0
	45	0.4	100.0	0

Table IVKerosene

	<u>% Water in Emulsion</u>	<u>% Emulsifier</u>	<u>% Emulsion</u>	<u>% Free Water</u>
20	5	0.1	99.8	0.20
	10	0.1	99.75	0.25
	15	0.1	99.75	0.25
	45	0.1	100.0	0
25	5	0.2	99.8	0.20
	10	0.2	99.75	0.25
	15	0.2	100.0	0
	45	0.2	100.0	0
30	5	0.4	100.0	0
	10	0.4	99.95	0.05
	15	0.4	99.95	0.05
	30	0.4	100.0	0
35	45	0.4	100.0	0

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Table V#2 Fuel Oil

	<u>% Water in</u> <u>Emulsion</u>	<u>%</u> <u>Emulsifier</u>	<u>%</u> <u>Emulsion</u>	<u>%</u> <u>Free Water</u>
5	5	0.4	99.95	0.05
	10	0.4	100.0	0
	15	0.4	100.0	0
	30	0.4	100.0	0
	45	0.4	100.0	0

- 10 The results illustrate the fact that increased emulsification can be achieved using increased levels of the emulsification system used, regardless of the light fuel oils with which the emulsion is formed.

Example V

- 15 The effect on NO<sub>x</sub> emissions of using the inventive emulsions is illustrated by firing a gas turbine using #2 fuel oil (baseline) and a 55% water-in-oil emulsion comprising 0.26% of emulsifier 3 (emulsion). The wattage, nitrogen oxides levels (further broken down into
- 20 NO and NO<sub>2</sub>), carbon monoxide levels, excess oxygen and temperature for each run are set out in Table VI.

TABLE VI

	<u>Megawattage</u>	<u>% O<sub>2</sub></u>	<u>Temp</u> <u>(°F)</u>	<u>NO<sub>x</sub></u>	<u>NO</u>	<u>NO<sub>2</sub></u>	<u>CO</u>
25 Baseline	33	16.9	712	71	59	12	90
Baseline	32.5	17.0	716	84	71	13	80
Emulsion	32.0	17.0	732	40	26	14	130

It should be noted that firing the turbine with an

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emulsion according to the present invention results in significant reductions in NO and total NO<sub>x</sub> as compared with baseline. In addition, although fired at a lower wattage, the emulsion resulted in a higher effluent  
5 temperature (indicating more efficient combustion) as compared with baseline.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail  
10 all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is  
15 defined by the following claims.

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Claims

1. A fuel oil composition effective for reducing the emission of nitrogen oxides from a turbine, comprising an emulsion which comprises water and a light crude naphtha fuel oil, said emulsion further comprising an  
5 emulsification system which comprises:
  - a) about 25% to about 85% of an amide;
  - b) about 5% to about 25% of a phenolic surfactant;  
and
  - c) about 0% to about 40% of a difunctional block  
10 polymer terminating in a primary hydroxyl group.
2. The composition of claim 1, wherein said light crude naphtha fuel oil comprises distillate fuels, #2 oil, kerosene, jet fuels, and diesel fuels.
3. The composition of claim 2, wherein said amide comprises an alkanolamide formed by condensation of a hydroxyalkyl amine with an organic acid.
4. The composition of claim 2, wherein said phenolic surfactant comprises an ethoxylated alkylphenol.
5. The composition of claim 4, wherein said ethoxylated alkylphenol comprises ethylene oxide nonylphenyl.
6. The composition of claim 2, wherein said difunctional block polymer comprises propylene oxide/ethylene oxide block polymer.
7. The composition of claim 4, wherein said emulsification system further comprises from 0% to about 30% of a light crude naphtha fuel oil selected from the group

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consisting of distillate fuels, #2 oil, kerosene, jet  
5 fuel, and diesel fuel.

8. The composition of claim 1, which further comprises  
up to about 85% water-in-fuel oil.

9. The composition of claim 8, wherein said  
emulsification system is present in an amount of about  
0.05% to about 5.0% by weight.

10. An emulsification system for a water and light crude  
naphtha fuel oil emulsion, said emulsification  
comprising:

- a) about 25% to about 85% of an amide;
- 5      b) about 5% to about 25% of a phenolic surfactant;  
and
- c) about 0% to about 40% of a difunctional block  
polymer terminating in a primary hydroxyl group.

11. The emulsification system of claim 10, wherein said  
amide comprises an alkanolamide formed by condensation of  
a hydroxyalkyl amine with an organic acid.

12. The emulsification system of claim 10, wherein said  
phenolic surfactant comprises an ethoxylated alkylphenol.

13. The emulsification system of claim 12, wherein said  
ethoxylated alkylphenol comprises ethylene oxide  
nonylphenyl.

14. The emulsification system of claim 10, wherein said  
difunctional block polymer comprises propylene  
oxide/ethylene oxide block polymer.



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15. The emulsification system of claim 12, which further comprises from 0% to about 30% of a light crude naphtha fuel oil selected from the group consisting of distillate fuels, #2 oil, kerosene, jet fuel, and diesel fuel.

## INTERNATIONAL SEARCH REPORT

PCT/US92/08083

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10L 1/32  
US CL :44/301, 302

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,162,143 (Yount III) 24 July 1979, see claim 6.	1-15
Y	US, A, 4,173,455 (Fodor et al) 06 November 1979, see abstract.	1-15
Y	US, A, 4,832,802 (Beinke et al) 10 May 1983, see claim 1.	1-15
Y	US, A, 4,770,670 (Hazbun et al) 13 September 1988, see column 5, lines 24-30 and 51-55.	1-15
A	US, A, 3,281,438 (Johnson) 25 October 1966, see column 2, lines 1-47.	1-15

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

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03 DECEMBER 1992

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